Grant CHE-85-14495. The SQUID magnetometer at the University of Southern California was also purchased with the aid of an NSF grant.

Supplementary Material Available: Tables listing experimental details of the crystallographic study, hydrogen atomic positional parameters, anisotropic thermal parameters, bond distances, bond angles, and observed magnetic susceptibilities (13 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, D-006,
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Insertion of a Copper Nitrene into a C–H Bond To Form Bis(2-(phenylamino)-1,10-phenanthrolinato)dicopper(I): A Short Cu–Cu Distance with No Bond?

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The complex $Cu(phen)Cl_2$ (phen = 1,10-phenanthroline) reacts with $[Li(THF)_x]_2[PhNN{=}NNPh]$ (I) to yield the copper(I) dimer $[Cu(2\text{-}NPh\text{-}phen)]_2$ (II), formed by insertion of NPh into the ortho C–H bond of phenanthroline. Complex II crystallizes in the monoclinic crystal system at 294 K with space group $P2_1/n$ and lattice constants $a = 5.551$ (2) Å, $b = 13.700$ (5) Å, $c = 17.865$ (6) Å, $\beta = 97.85$ (3)°, and $Z = 2$. Refinement of the structure led to an R factor of 0.055 for 1399 reflections with $I > 3\sigma(I)$ and 82 least-squares parameters. In the structure of II, the coordination sphere of Cu approximates a square plane with a Cu–Cu separation of 2.600 (2) Å. Each square plane shares a common vertex. Complex II is inert to unsaturated ($PhN{=}NPh$, $PhC{\equiv}CPh$, $CH_2{=}CHCH_2Cl$) and amine (CH_3NH_2) ligands. Electrochemical studies show that II undergoes one chemically reversible oxidation, forming the mixed-valence complex, and a second chemically irreversible oxidation. SCF–Xα–DV calculations of model complexes for II and for a monomeric fragment suggest a repulsive interaction between the d^{10} Cu(I) centers. The dinuclear configuration appears to be dictated by the 2-(phenylamino)-1,10-phenanthroline(1–) ligand.

Introduction

Since 1967, several transition-metal tetrazene complexes have been reported, including derivatives of Ni, Pt, Co, Rh, Ir, and Fe.[1] We recently prepared[2,3] several transition-metal tetrazene complexes from the readily available tetrazenido dianion of I (eq 1).[3]

$$PhNHLi + PhN_3 \xrightarrow[THF]{} Ph(H)NN{=}NN(Ph)Li \xrightarrow[THF]{^nBuLi} \underset{\textstyle I}{[Li(THF)_x]_2[PhNN{=}NNPh]} \quad (1)$$

This reagent has permitted the synthesis of tetrazene complexes of Ni, Pd, and Pt, which allows a comparison of metal–tetrazene bonding within a triad. This reagent has also been applied to the preparation of main-group tetrazene compounds[4] and the first early-transition-metal tetraazabutadienes.[5] The results of the above studies prompted us to investigate the possibility of forming a Cu–tetrazene complex with I, since they are unknown for this metal. Herein we report the unexpected results from the reactions between I and a dihalo Cu(II) complex.

Experimental Section

Reactions were performed with standard Schlenk and cannula filtration techniques under a nitrogen atmosphere. Solids were manipulated in a Vacuum Atmospheres glovebox equipped with an HE-493 dry chain. Glassware was either oven-dried or flame-dried before use. Benzene, diethyl ether, toluene, THF, and hydrocarbon solvents were refluxed over sodium or potassium benzophenone ketyl and distilled under nitrogen or by vacuum transfer. Dichloromethane and pyridine were distilled over CaH_2 and BaO, respectively. $CDCl_3$ was freeze–pump–thaw degassed before use and stored under nitrogen. The dianion of I, $[Li(THF)_x]_2[PhNN{=}NNPh]$,[3] and $Cu(phen)Cl_2$[6] were prepared by literature methods.

Table I. Crystallographic Data and Summary of Data Collection and Structure Refinement for II

chemical formula	$C_{36}H_{24}N_6Cu_2$	β, deg	97.85 (3)
fw	698.51	V, Å^3	1346 (1)
cryst syst	monoclinic	ρ_{calc}, g cm^{-3}	1.65
space group	$P2_1/n$	μ, cm^{-1}	16.2
a, Å	5.551 (2)	Z	2
b, Å	13.700 (5)	$R(F_o)$	0.055
c, Å	17.865 (6)	$R_w(F_o)$	0.061

Cyclic voltammetric studies were carried out by using a BAS 100 electrochemical analyzer equipped with a Houston Instruments DMP-40 plotter. Solutions (CH_2Cl_2) were ca. 1 mM in the metal complex and contained 0.1 M $[^nBu_4N][PF_6]$ as supporting electrolyte. For these measurements, a conventional three-electrode cell (Pt-disk working electrode, Pt-wire auxiliary electrode, Ag-wire pseudoreference electrode) was employed. Instrumental IR compensation was applied in all measurements. The $E^{\circ\prime}$ value for the Cp_2Fe/Cp_2Fe^+ couple was 0.59 V at 300 mV/s in the cell. ^1H NMR were obtained with either a Varian EM-390 or a General Electric-QE 300-MHz spectrometer. IR spectra were recorded with an IBM IR/32 spectrometer. UV spectra were recorded with an IBM UV 9420 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

Synthesis of Bis(2-(phenylamino)-1,10-phenanthrolinato)dicopper(I) (II). Addition of 0.5 g of I in 30 mL of pyridine to a stirred green slurry of 0.5 g (1.59 mmol) of $Cu(phen)Cl_2$ in 30 mL of pyridine gave a dark red solution. After 8 h the solution was filtered, concentrated under vacuum, and layered with diethyl ether to yield purple crystals. These crystals were washed with THF (20 mL × 3) and Et_2O (20 mL × 2) and dried under vacuum to yield 0.31 g (30%) of II. ^1H NMR ($CDCl_3$): δ 7–8 (m, phen). Anal. Calcd for $C_{36}H_{26}N_6Cu_2$: C, 64.58; H, 3.89; N, 12.55. Found: C, 64.12; H, 3.25; N, 12.89. Mp: 264–266 °C. UV (THF): 310 nm (38 000 M^{-1} cm^{-1}), 404 (23 600), 460 (5500).

X-ray Structure Determination. X-ray data were collected with use of a Nicolet R3m/V automated diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. Crystal and intensity data are given in Table I. The orientation matrix and unit cell parameters were determined from 20 machine-centered reflections with $15 < 2\theta < 30°$. Intensities of three check reflections were monitored after every 100 reflections during data collection. The ω–2θ scan procedure was used to collect 2506 unique data. The scan range was 0.6° below K_{α_1} to 0.6° above K_{α_2}. Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied.

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0020-1669/90/1329-1659$02.50/0

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Temperature Factors ($\times 10^3$ Å^2) for II

	x	y	z	U(eq)
Cu	1833 (2)	4518 (1)	5353 (1)	37 (1)
N(2)	1421 (10)	5377 (3)	6209 (3)	28 (1)
C(21)	−196 (13)	6118 (4)	6172 (3)	28 (2)
C(22)	−300 (14)	6682 (5)	6859 (4)	40 (2)
C(23)	1108 (15)	6464 (5)	7515 (4)	40 (2)
C(24)	2932 (14)	5711 (4)	7531 (4)	33 (2)
C(25)	2976 (14)	5205 (4)	6852 (3)	30 (2)
N(3)	5145 (11)	4109 (4)	6133 (3)	32 (1)
C(31)	6976 (15)	3522 (5)	6088 (4)	41 (2)
C(32)	8710 (15)	3294 (5)	6707 (4)	42 (2)
C(33)	8578 (15)	3707 (5)	7383 (4)	40 (2)
C(34)	6648 (14)	4341 (4)	7471 (4)	35 (2)
C(35)	4937 (13)	4532 (5)	6820 (3)	32 (1)
C(100)	4582 (14)	5483 (5)	8191 (4)	41 (2)
C(200)	6342 (15)	4822 (5)	8159 (4)	40 (2)
N(1)	1543 (11)	3682 (4)	4477 (3)	30 (1)
C(12)	5088 (9)	2744 (3)	4158 (2)	32 (2)
C(13)	6665	1954	4305	38 (2)
C(14)	6273	1269	4854	37 (2)
C(15)	4304	1376	5255	39 (2)
C(16)	2727	2167	5108	34 (2)
C(11)	3119	2851	4560	28 (1)

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for II

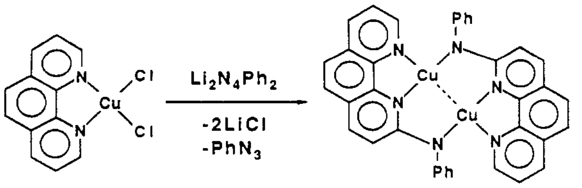
Bond Distances			
Cu–Cu(a)	2.600 (2)	Cu–N(3)	2.221 (5)
Cu–N(1)	1.928 (5)	N(1a)-C(21)	1.325 (8)
Cu–N(2)	1.967 (5)		
Bond Angles			
N(1)–Cu–N(2)	168.6 (2)	Cu–N(2)–C(25)	115.2 (4)
N(1)–Cu–N(3)	109.2 (2)	Cu–N(2)–C(21)	124.0 (4)
N(2)–Cu–N(3)	80.7 (2)	Cu–N(2)–C(11)	114.0 (3)
Cu–N(3)–C(35)	106.9 (4)		

A dark red crystal of II, shaped as a block, of approximate dimensions 0.3 × 0.4 × 0.5 mm, was mounted on a glass fiber for crystal data and intensity data collection. The unit cell parameters and systematic absences, $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$), unambiguously indicated the space group $P2_1/n$. All calculations were carried out on a Microvax II computer with use of the SHELXTL PLUS program package.

Refinement of 82 least-squares parameters for 1399 reflections of $I > 3\sigma(I)$ converged to a GOF of 1.68. The largest peak in the final difference Fourier map was 0.58 e/Å^3. Final atomic positional parameters for non-hydrogen atoms are shown in Table II; anisotropic thermal parameters, complete tables of bond distances and angles, hydrogen atom coordinates, and tables of observed and calculated structure factors are available as supplementary material.

Results

The d^{10}–d^{10} Cu(I) dimer, II, was synthesized by the reaction between the dianion of I and Cu(phen)Cl$_2$ (eq 2). Phenyl azide was observed in the IR spectrum as a byproduct of the reaction, and complex II did not exhibit N–H absorptions in its IR spectrum.



(2)

II

The molecular structure and atomic numbering scheme obtained from a single-crystal X-ray study of II is shown in Figure 1. The coordination sphere of Cu can be described as a square plane, since the bond angle sum around Cu (Table III) is almost 360° (358.9°) and all the atoms except for the two *N*-phenyl rings adopt a nearly planar geometry (average displacement from the molecular plane <0.103 Å). The overall planarity of the molecule leads to a herringbone stacking pattern down the *a* axis of the unit cell (Figure 2). The closest intermolecular Cu–Cu distance along a stack is 5.551 Å. The two phenyl rings are twisted out of the plane with a dihedral angle of 67°. The Cu–N(1) (1.928 (5) Å), Cu–N(2) (1.967 (5) Å), and Cu–N(3) (2.221 (5) Å) distances suggest that N(3) is not optimally oriented for donation to the second Cu, and this is evident in Figure 1.

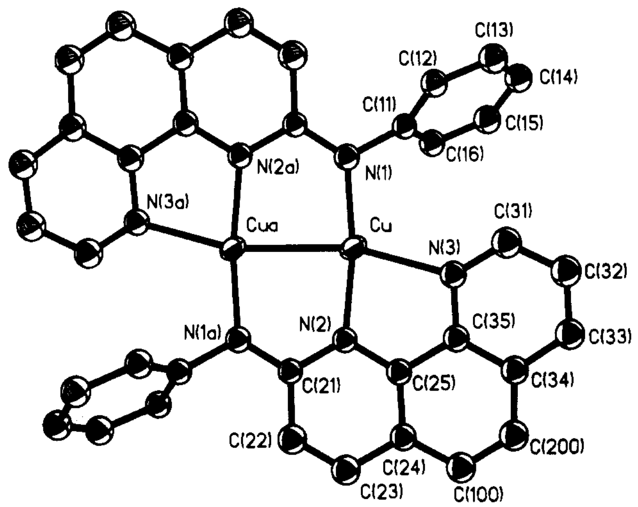


Figure 1. ORTEP drawing of complex II, showing the labeling scheme and 50% probability thermal ellipsoids. Symmetry equivalent atoms (denoted by an a) are generated by the crystallographic inversion center located midway between Cu and Cu(a).

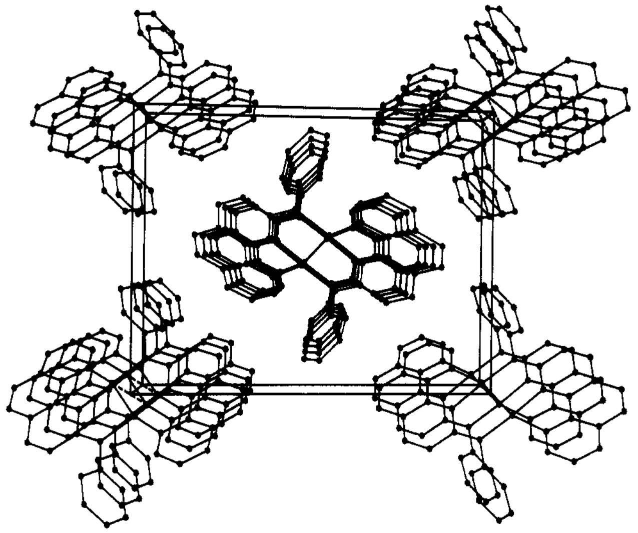


Figure 2. Unit cell packing diagram for II viewed down the *a* axis.

Results of cyclic voltammetry studies on II are displayed in Figure 3. Two main features were observed in CH$_2$Cl$_2$ at 20 °C: one chemically reversible oxidation at 0.167 V and one chemically irreversible oxidation at 1.025 V vs a Ag-wire pseudoreference electrode. The electrochemical data suggest that a monocation II$^+$ containing Cu(I) and Cu(II) is stable on the cyclic voltammetry time scale and a dication II^{2+} containing two Cu(II)'s is unstable, with the assumption that oxidation occurs at the metal centers. Attempts to characterize II$^+$ by EPR spectroscopy in a bulk coulometry experiment were not successful because of instability of II$^+$ on the preparative time scale.

Discussion

The formation of II according to eq 2 suggests that fragmentation of I occurs according to Scheme I. A complex similar to A of Scheme I was proposed as an intermediate in the preparation of PhNN=NN(Ph)SiMe$_2$, PhNSiMe$_2$N(Ph)SiMe$_2$, and PhN(SiMe$_2$Cl)$_2$ from the reaction between I and Me$_2$SiCl$_2$.[4] Insertion of a coordinated nitrene intermediate into an aromatic C—H bond

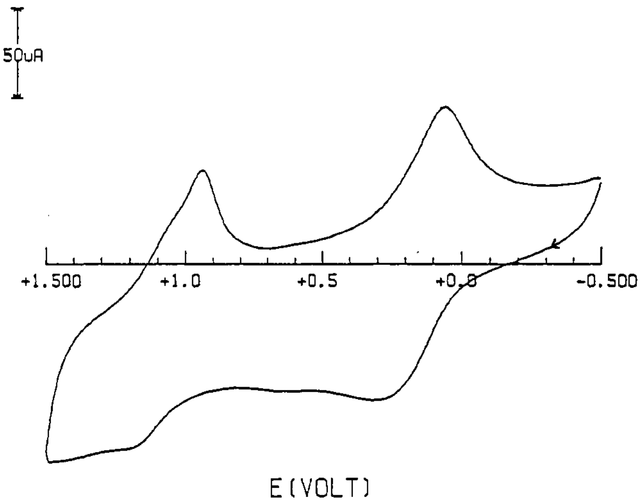
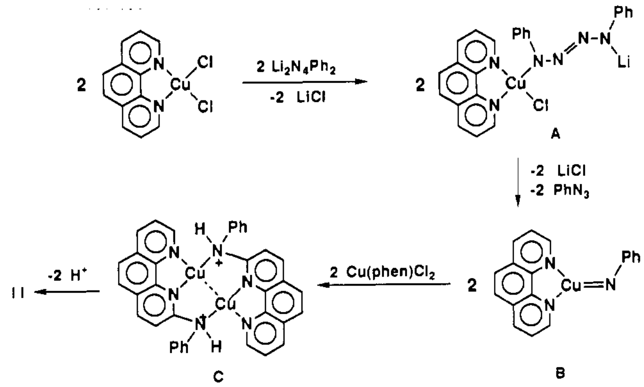


Figure 3. Cyclic voltammogram of II in CH_2Cl_2/0.1 M [$^n Bu_4N$][PF_6] at 300 mV/s vs a silver-wire reference electrode.

Scheme I



has been observed for (η^5-C_5H_5)Co(NPh)$_2$, generated by photolysis[7] of (η^5-C_5H_5)Co(1,4-Ph_2N_4), and for *cis*-Os(η^4-HBA-B)-(NPh)$_2$.[8] Thus, species B is a reasonable intermediate and can be converted to II by oxidative deprotonation, as shown. In the silicon system mentioned above, the evidence for such a species derives from its dimerization to the cyclic dimer PhNSiMe$_2$N(Ph)SiMe$_2$. These insertion reactions of metal nitrenes all involve metals in a high formal oxidation state [(Co(V), Os(VIII), and Cu(III)]. Several tridentate phenanthroline derivatives have been reported,[9] and one crystal structure containing such a derivative, [Ni($C_{19}H_{14}N_4$)$_2$(BF_4)$_2$], was determined.[10] These ligands have been prepared from the nucleophilic attack of a donor-atom-containing substituent on 2-chloro-1,10-phenanthroline.[9]

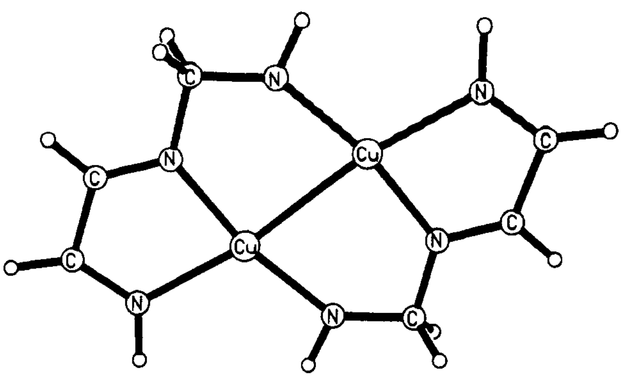


Figure 4. Model complex used in the Xα calculations.

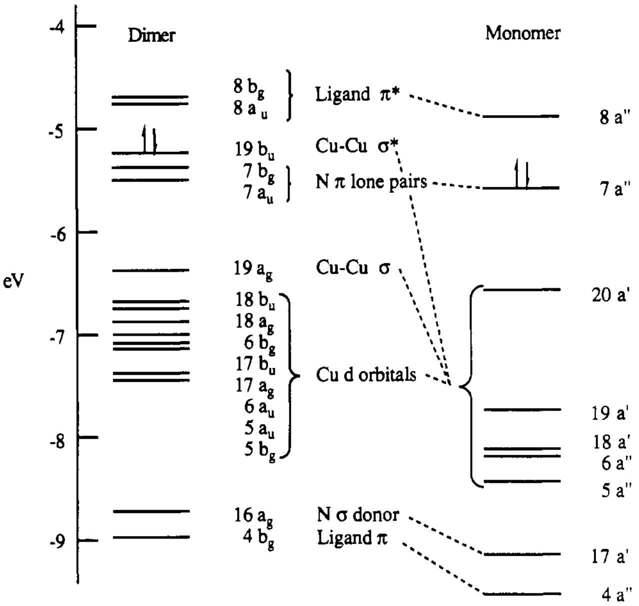


Figure 5. Results of SCF-Xα-DV calculations for the model Cu dimer complex and the tricoordinate monomeric fragment Cu(NH_2)(N(CH_3)CHCHNH) obtained by breaking the CH_2-NH bridging bonds and capping with hydrogens.

The short Cu-Cu distance of 2.600 (2) Å in II approaches the Cu-Cu distance in Cu metal (2.55 Å[11]). The metal centers in II have the formal oxidation state +1. Several other polynuclear Cu(I) complexes are known to contain short Cu-Cu contacts (2.35-2.60 Å).[11,12] Although there are no examples of a Cu-Cu bond without a supporting bridging ligand, s + p_z + d_{z^2} mixing could result in an attractive interaction,[13] which is similar to the explanation[14] proposed for the oligomerization of square-planar d^8 Rh(I) complexes. There is a fundamental difference between II and other d^{10}-d^{10} dimers in that II adopts a geometry where two square planes share a vertex, whereas other examples of Cu(I)-Cu(I) bonding[13] involve face to face overlap. Thus an antibonding metal-ligand orbital ($d_{x^2-y^2}$ of the square-planar fragment) would have to be used to form the metal-metal bond in II. Because of the interest in interactions of d^{10}-d^{10}-bonded complexes,[13,15,16] we examined the model complex for II, shown in Figure 4, by SCF-Xα-DV calculations.[17] Results are summarized in Figure 5.

Although the simple computational model complex used permits only an approximate placement of ligand π orbitals, the MO scheme should be qualitatively valid. A comparison of the changes

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that occur when two hypothetical Cu(I) monomers are brought together to allow the Cu–Cu interaction is especially informative (Figure 5). A single orbital, $19b_u$, rises high above the other nine filled Cu d orbitals to become the highest occupied molecular orbital (HOMO). The solution spectrum of II exhibits a low-energy absorption (460 nm, $\epsilon = 5500\ M^{-1}\ cm^{-1}$) that can be assigned to a Cu–Cu (σ^*) → ligand π^* transition, which results from destabilization of the Cu d orbital to higher energy in the dimer. There is no evidence in the calculations that the Cu–Cu interaction leads to an enhanced stability. In fact, there appears to be a net destabilization of the entire Cu d band because of the repulsive interaction between the two d^{10} metal centers. Unlike extended Hückel calculations for other Cu(I)[13] dimers, the Xα results show <3% mixing of 4s and 4p character into the Cu–Cu $19b_u\ \sigma^*$ orbital. The $19a_g\ \sigma$ orbital exhibits greater (15%) 4s + 4p hybridization; however, it is also destabilized when compared to the d band in the monomeric fragment (Figure 5). Extensive 3d–4s4p mixing has been postulated[13] to result in attractive Cu–Cu interactions. In these cases, as noted above, the molecular geometry differs from II. Our calculations resemble an SCCC MO study[18] of a $Cu_8S_{12}^{4-}$ cluster where 3d–4s4p hybridization and Cu–Cu bonding did not occur.

At present, the examples of d^{10}–d^{10} dimers without supporting bridging ligands are restricted to compounds of third-row metals such as Pt(0). Because the d–sp energy separation decreases for the third-row late transition metals, they exhibit a greater tendency to undergo oxidative addition reactions [e.g. Pt(0) to Pt(II)] and the dsp hybridization necessary for metal–metal bond formation. To illustrate this point, we contrast the spectroscopic energies[19] of the $3d^94s^1$ (^3D) and $3d^94p^1$ ($^3P_2{}^0$) atomic states in Cu^+ at 2.72 and 8.24 eV above the $3d^{10}$ (^1S) ground state with the case of Pt^0, where the $4d^96s^1$ configuration is the ground state and the $5d^{10}$ (^1S) and $5d^96p^1$ ($^2D_{5/2}$) states occur at 0.76 and 4.04 eV, respectively. Although these values are for monoatomic species in the gas phase, reduced dsp hybridization (or configuration interaction) and reduced metal–metal bond strength can be expected for Cu(I) dimers as compared to Pt(0) d^{10} dimers, because of the large energetic differences in the parent atomic states. Because neither extended Hückel theory nor Xα theory can be expected to reliably model the precise amount of 3d–4s4p hybridization, we believe the extent of metal–metal bonding in Cu(I) systems with bridging ligands will be difficult to quantify. The results obtained for II, whose structure forces overlap of two filled antibonding orbitals, suggest that quite short Cu(I)–Cu(I) distances can be enforced without appreciable metal–metal bonding.

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Supplementary Material Available: Tables of bond distances, bond angles, anisotropic displacement parameters, and hydrogen atom coordinates (6 pages); tables of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Preparation and Reactions of Sulfido and Persulfido Complexes of (Pentamethylcyclopentadienyl)tungsten

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Received October 25, 1989

Boron sulfide and hydrogen sulfide react with tungsten–oxo compounds to yield $(\eta^5\text{-}C_5Me_5)W({=}S)_2R$ (**1a**, R = Me; **1b**, R = CH_2SiMe_3), $(\eta^5\text{-}C_5Me_5)W({=}S)(\eta^2\text{-}S_2)Me$ (**2a**), and $(\eta^5\text{-}C_5Me_5)W({=}O)(\eta^2\text{-}S_2)Me$ (**3**). Thiophiles such as PPh_3 and CN^- readily abstract sulfur from the persulfido complexes **2a** and **3**; however, the sulfido ligands of **1a** and **1b** are inert to abstraction under similar conditions. In the presence of oxidizing agents, **1a** undergoes intermolecular transfer of sulfur, giving **2a** and $(\eta^5\text{-}C_5Me_5)W({=}O)({=}S)Me$. Compound **1b** crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.967$ (2) Å, $b = 9.323$ (1) Å, $c = 18.092$ (3) Å, $V = 1843.8$ Å^3, and $Z = 4$. Anisotropic refinement of all non-hydrogen atoms and inclusion of hydrogen atoms at calculated positions converged to the residuals $R_1 = 0.027$ and $R_2 = 0.035$.

Introduction

The chemistry of molybdenum–sulfido (Mo=S) and molybdenum–persulfido [$Mo(\eta^2\text{-}S_2)$] systems is pertinent to the understanding of a number of biological and catalytic processes. The presence of a Mo=S unit in the active sites of numerous molybdenum enzymes has been demonstrated via EPR and EXAFS techniques.[1] The involvement of persulfido ligands in biological systems as reaction intermediates has been postulated.[2] In addition, compounds containing $Mo(\eta^2\text{-}S_2)$ units have been employed in model studies[3] of the catalytic surface responsible for hydrodesulfurization,[4] a heterogeneous process in which sulfur derived from petroleum products is converted to hydrogen sulfide in the presence of hydrogen. The literature of the last decade reflects a growing interest in sulfur complexes of molybdenum in its higher oxidation states as models for the structures and reactivity of these biochemical and catalytic systems.[3,5-10] The analogous chemistry

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